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# HIPIMS AND MPP SPUTTERED TA FILMS USING I_PVD TECHNOLOGY

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## Keywords
HIPIMS, MPP, Magnetron Sputtering, Tantalum

## Abstract
HIPIMS (high power impulse magnetron sputtering) process utilizing I-PVD technology can produce high ionization, high flux, and high intensity plasma. The metal ions from the target can be used for substrate etching and for the deposition of improved quality coatings. MPP (modulated pulse power) is a variation of HIPIMS that increases the deposition rate through modulation of the pulse shape, intensity, and duration. In MPP, the pulse shape and duration and plasma perturbations affect the degree of ionization of the plasma. In this work, HIPIMS and MPP techniques were investigated to deposit tantalum coatings on steel substrates. The film properties, including topography, microstructure, hardness, phase, residual stress and adhesion were characterized. A phase transformation from hard tetragonal tantalum to soft bcc tantalum was observed as a function of substrate bias voltage.

## Contents

## Introduction

Electroplated high contraction chrome (HC Cr) has been used in a variety of applications to protect the substrates from wear, erosion, corrosion, and surface oxidation. The pre-deposition cleaning and the chrome electroplating processes produce hexavalent chrome and toxic chemicals detrimental to the environment. HC Cr also possesses extensive as-deposited and firing-induced cracks, accelerating coatings and substrate degradation and failure. There has been intense search for environmental friendly new materials and new deposition processes to replace electroplated chrome.

For high temperature wear and erosion applications, refractory metal tantalum has been investigated. Tantalum coatings deposited from high temperature molten salt solution onto 20mm riffled liners exhibited excellent wear and erosion properties [1, 2]. Tantalum was deposited on 45mm inside-diameter rifled barrels using a triode sputtering system [3-6]. Properties of magnetron sputtered Ta coatings with bcc and tetragonal phase were investigated [7]. An in-situ magnetron sputtering system with real time XRD was constructed to study phase and texture evolution of sputtered tantalum thin films [8]. Tantalum coatings up to 200μm have been deposited on the interior surfaces of 120 mm inside-diameter steel cylinders, with a thin electroplated HC chromium adhesion interface layer using cylindrical magnetron sputtering systems [9-11]. Tantalum alloys have also been deposited on the interior surfaces of cylindrical structure using explosive bonding technologies [12].

In plasma enhanced physical deposition technology via magnetron sputtering, an external electron source was used to generate intense secondary plasma in addition to magnetron generated plasma [13]. The increased ion bombardment from high intensity plasma and biasing can deposit dense, adhesive, quality tantalum coatings directly on A723 steel [14]. Plasma enhanced tantalum coatings up to 286μm deposited on A723 steel were tested using groove, pulsed laser heating, and vented erosion simulator adhesion testing. The coatings demonstrated superior performance compared to electroplated chromium coatings under the same testing conditions [14, 15]. A plasma-enhanced cylindrical magnetron was constructed with increased plasma intensity in the cylindrical geometry [16].

HIPIMS or HPPMS (high power pulsed magnetron sputtering) methods utilize I-PVD technology is being considered for potential high temperature wear and erosion applications. The technology was introduced in recently years to utilize high power pulses of short duration to ionize the target, and target ions can be used for deposition of coatings. The technology has been shown to improve coatings qualities compared to conventional DC magnetron sputtered films [17, 18]. Tantalum coatings were deposited in a trench with high depth to width aspect ratio using this technology: while DC magnetron deposited film was porous, rough, and directional, HIPIMS deposited tantalum was dense, uniform, with very good microstructure [19]. HIPIMS technology can

deposit dense, hard, oxidation-resistant, low friction, adhesive coatings to improve service life of coated components, and the technology is on the way to commercialization [20].

The MPP method is a variation of the HIPIMS-HPPMS process, allowing full control of magnetron plasma parameters at high power level. The long pulse duration and modulation of the cathode voltage during high power pulsed sputtering gives a high sputter deposition rate, which can exceed DC magnetron with the same average power level [21]. In this work, the HIPIMS-MPP methods using I-PVD technology were investigated to deposit tantalum coatings on steel substrates. It was shown that significant amount of tantalum and Ar ions were generated in the process for improved coatings deposition. The film properties were found to be a sensitive function of deposition parameters, such as the substrate bias voltage.

## Experimental Procedure

Flat A723 steel was cut into 2.5 cm x 1.2 cm x 2.3 cm samples, cleaned in alcohol and acetone and polished using 1 μm diamond paste. The Chemfilt SINEX 2.0-AS14 on a balanced magnetron was used to etch the steel surfaces and to deposit tantalum coatings [22]. The steel samples were cleaned ultrasonically for 5 minutes in acetone and 5 minutes in 2-isopropanol, prior to Ar and Ta etching: Argon gas pressure was 2 mTorr during Ta etch and Ta deposition; and 50 mTorr during Ar etch. Parameters for etching and deposition were: peak voltage 900 V, pulse length 50 μs, frequency 300 Hz; 510-520 W for etching and 550-570W for deposition. HIPIMS #4 used 10 min Ar, 30 min Ta etch at 1000v, HIPIMS #6 and HIPIMS-Slanted used 30 min Ta etch at 1000v. Tantalum deposition was made with negative bias of 50V for 60 minutes. Two serial TCR 600V/3A DC power supplies were used to provide the bias voltage. The deposition rate was ~2 μm/hr.

For the MPP tantalum depositions, the deposition parameters are listed along with the characterization results in Table 1. The substrate to magnetron distance was 10cm, MPP power supply was an Axia-100 with a 100 kW peak pulse power. The surface of the substrate steel was cleaned with RF sputter etch process (RF power, ~200 W, substrate bias, 700 V, sputter etch process time ~ 20 min). The magnetic field of the magnetron was ~300 G. Argon gas flow was 200 sccm that correspondent to 5 mTorr sputtering pressure. Target power density was approximately 0.37 kW/ cm2.

MPP tantalum deposition was first tested on silicon substrate in comparison with conventional DC magnetron sputtering at -30 volt bias using pulse shape 1. The same pulse shape was then used to deposit S1, S2, and S4 on tool steel samples at varying substrate bias voltage. The average power for MPP deposition was 1.5kW. The MPP deposition rate was ~18 μm/hr.

## Results

HIPIMS Tantalum Depositions

Fig. 1 shows the cross section of tantalum depositions using a Chemfilt SINEX 2.0-AS14 HIPIMS power supply on a balanced magnetron. The coatings with ~2 μm thickness were shown in two magnifications. Dense and uniform tantalum coatings deposited directly on A723 steel were observed. The coatings also showed good featureless microstructure. The deposition on the slanted A723 sample was performed to test the potential to deposit coatings on an object of complex geometry. It showed uniform coatings with slight thickness variation on the slanted edge. The slight difference in etching conditions for the samples (HIPIMS #4 at 10 min Ar, 30 min Ta, 1000v) and HIPIMS #6 and HIPIMS-Slanted (30 min Ta etch at 1000v) did not produce any difference in coatings microstructure. XRD phase and texture were characterized, but not presented here. The XRD data showed bcc α-Ta crystalline structure with Ta (110) preferred orientation in all coated A723 steel samples in this investigation, and no difference in crystalline structure was observed due to differences in etching conditions.

Fig. 2 shows the pulse shape used in the tantalum coatings deposition using MPP I-PVD method. The voltage pulse consisted of two stages. The low power stage was -500 V discharge voltage, and 16 A discharge current for 500 μs duration, the total power was 8 kW. In high power stage, the discharge voltage was -600 V and discharge current 48 A. The total power was 28.8 kW. The time duration for the high power stage was 1000 μs. The ion current during high power stage was about 1 A that correspondent to 143 mA/cm2 in the experiment.

Fig. 3 and 4 show the OES spectrums for DC Ta process in comparison with MPP Ta sputtering process. The conventional DC magnetron sputtering process with average power 2 kW did not show the presence of Ta ions (line 1) in the magnetron discharge. But MPP sputtering process shows the presence of Ta ions and Ar ions (line 2). The data show that the intensity of Ta lines reduced in pulsed process compare with DC process, but the intensity of $Ta^{+}$ increased in pulsed sputtering process compare with DC process.

Fig. 5 and 6 show the comparison of SEM microstructure of tantalum depositions for MPP method and DC magnetron sputtering depositions. During the sputtering process DC bias -30 V was applied to the substrate in both MPP and conventional DC sputtering. It was observed that as DC magnetron sputtered tantalum film had a columnar microstructure, the MPP film was very dense with near featureless microstructure.

As shown in Table 1, tantalum films were deposited as a function of bias voltage. Residual stress was measured using two-dimensional XRD technique. The coating hardness and residual increased with bias voltage as expected. Fig. 7 and 8 show respectively the microstructure and topography of tantalum coatings as a function of substrate bias voltage. In Fig. 7, SEM is shown for- 1) Sample S1 deposited at -30 V (top), 2) Sample S2 deposited at -40V (middle), 3) Sample S4 deposited at -50V at two locations (bottom two figures). The samples were etched to show the microstructure detail. Harder β-Ta is shown in lighter color, as softer α-Ta is shown in

darker color. S1 shows severely cracked β-Ta in α-Ta coatings due the high residual stresses. S2 shows α-Ta coatings mixed with β-Ta coatings. S4 shows predominately α-Ta coatings. Only a small trace of β-Ta was observed. In Fig. 8, SEM topography is shown for S4: The left figure is S4 at 15,000X, showing very dense and smooth coatings. The middle figure is S4 deposited by MPP at 8,000X. The right figure is DC magnetron sputtered tantalum coatings with no bias at 8,000X [10]. MPP show dense, smooth, small grained tantalum films compared to DC magnetron deposited tantalum films.

Fig. 9 shows the XRD comparison for S1, S2, and S4. Fig. 6a shows the Debye rings for the samples, as Fig. 9 shows the diffraction patterns. Sample S1 shows α-Ta with Ta (110) preferred orientation, and highly textured β-Ta with intense Ta (002) reflections. Samples S2 and S4 showed predominately α-phase Ta coatings.

## Discussion

Plasma enhanced magnetron system using secondary plasma generated by an external filament increased the current density by 25 fold compared to DC magnetron. Coatings deposited using the system showed superior wear and erosion performance compared to electroplated chromium in high temperature wear and erosion testing [14, 15]. This is due to the fact that increased ion bombardment in the new process can produce dense, adhesive, crack-resistant coatings with less columnar microstructure. However, in the cylindrical geometry, a filament or an antenna to generate the external plasma can cast shadows on the substrate surfaces. HIPIMS-MPP using I-PVD technology may provide the solution for this problem since it can provide high ionization, high flex, high current density only by installing high power pulsed magnetron power supplies. This current work tests HIPIMS-MPP techniques in planar magnetron geometry; but it can be implemented in the cylindrical geometry to coat the bore surfaces.

Plasma-enhanced magnetron sputtering deposition using HIPIMS-MPPS techniques in this work showed that very dense small-grained coatings can be deposited which also have less columnar microstructure compared to DC magnetron deposited coatings. More metal and argon ions can improve coating qualities, including density, hardness, microstructure, and crack-resistance. However, the enhanced process can also increase residual stresses, as shown by the high compressive residual stresses observed in Table 1. High residual stresses can cause buckling, cracking, peel-off, and coating delamination. On the other hand, ion etching using metal and argon ions can clean the surfaces, providing a very clean substrate for good bonding, which counters the detrimental effects of high residual stresses.

Proper choices of deposition parameters are critical to improving the coatings properties. In this work, it was shown that substrate bias significantly affected the tantalum phase formation, and that increasing bias voltage

increased the bcc α-phase tantalum contents in the coatings. Tantalum phase was under extensive investigation, and it is believed that phase is related to ion bombardment energy [23]. It has been shown that when pre-heating the substrate to ~300°C temp prior to deposition results in all bcc α-Ta coatings [10, 11, 24].

## Conclusion

1) HIPIMS-MPP using I-PVD technology can generate significant more metal and argon ions in comparison to DC magnetron, which can be used to control Ta film structure.

2) In the MPP deposition, changing DC substrate bias from -30 V up to -50 V, changed crystalline structure of Ta from tetragonal to desired bcc phase.

3) HIPIMS-MPP processes can deposit dense, uniform, adhesive bcc phase Ta films on steel with good microstructure.

4) Technology can be applied to coat ordnance components against wear-erosion-corrosion.

5) Implementation in cylindrical geometry necessary for barrel coating applications.

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**Table 1: MPP Tantalum Deposition Parameters and Characterization Results**

| Sample | Deposit Time (min) | Bias Voltage (V) | Pulse Shape | Thick (μm) | Phase | Residual Stress (MPa) | Hardness (HK50) |
|---|---|---|---|---|---|---|---|
| S1 | 180 | -30 | 1 | 20 | β + α | -980 ± 312 | |
| S2 | 180 | -40 | 1 | 17 | α + β | -1,382 ± 158 | 504 |
| S4 | 180 | -50 | 1 | 16 | α | -1,516 ± 183 | 581 |

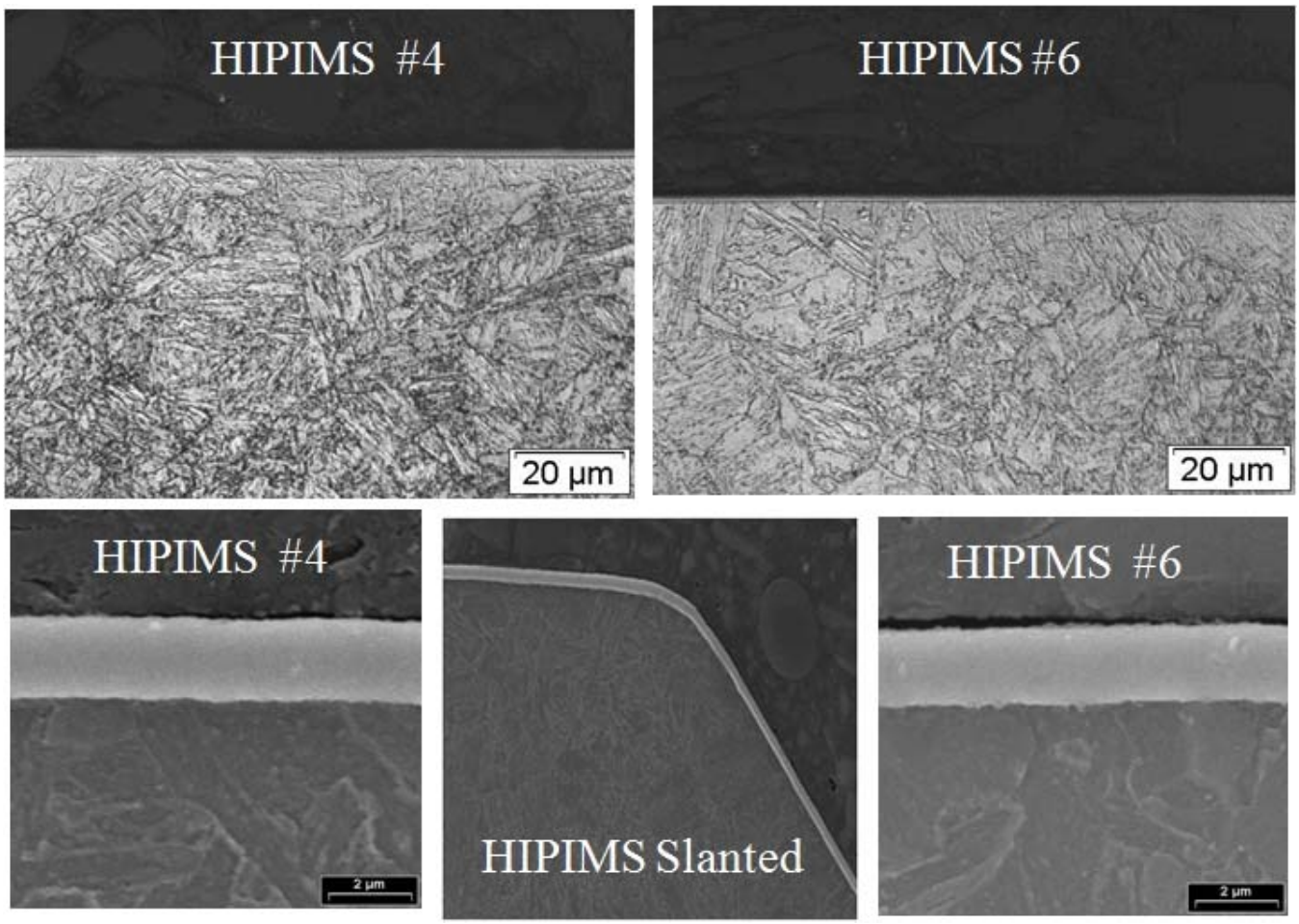


**Figure 1: SEM microstructure of HIPIMS Ta films of ~2µm thickness showing dense and uniform coatings on A723 steel. The deposition was performed using a using CHEMFILT SINEX power supply [22].**

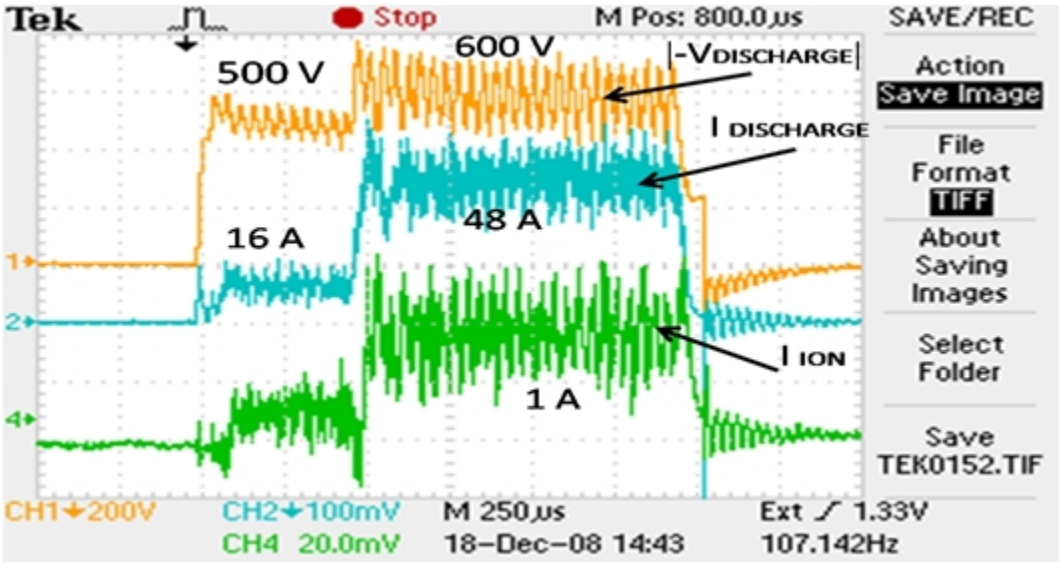


**Figure 2: Waveform characteristics of Pulse 1 used in the MPP deposition of Ta films, showing: discharge voltage (top line), discharge current (middle line), and substrate ion current (bottom line). The deposition was performed using a Zpulser AXIA-100 power supply.**

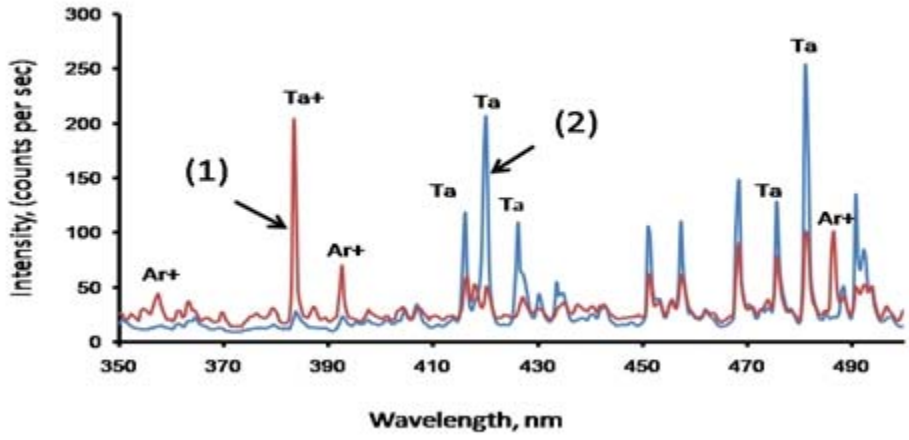


**Figure 3: OES for wavelength range 200 nm to 350 nm**

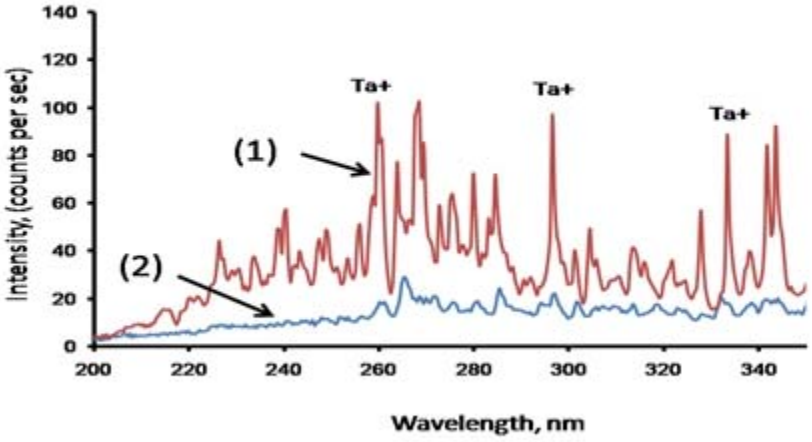


**Figure 4: OES for wavelength range of 350 nm to 500 nm.**

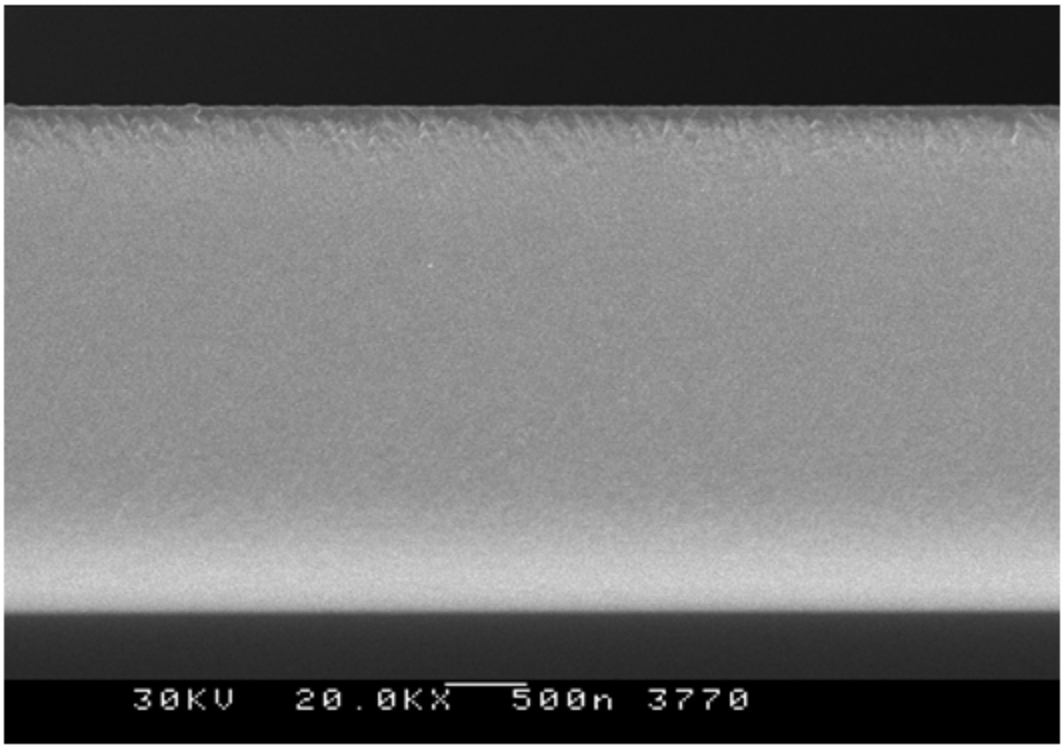


**Figure 5: SEM microstructure comparison of Ta depositions using the MPP process using Pulse 1 and conventional DC sputtering process at -30V substrate bias: MPP deposited Ta film. ; Fig. 4b shows DC magnetron deposited Ta film.**

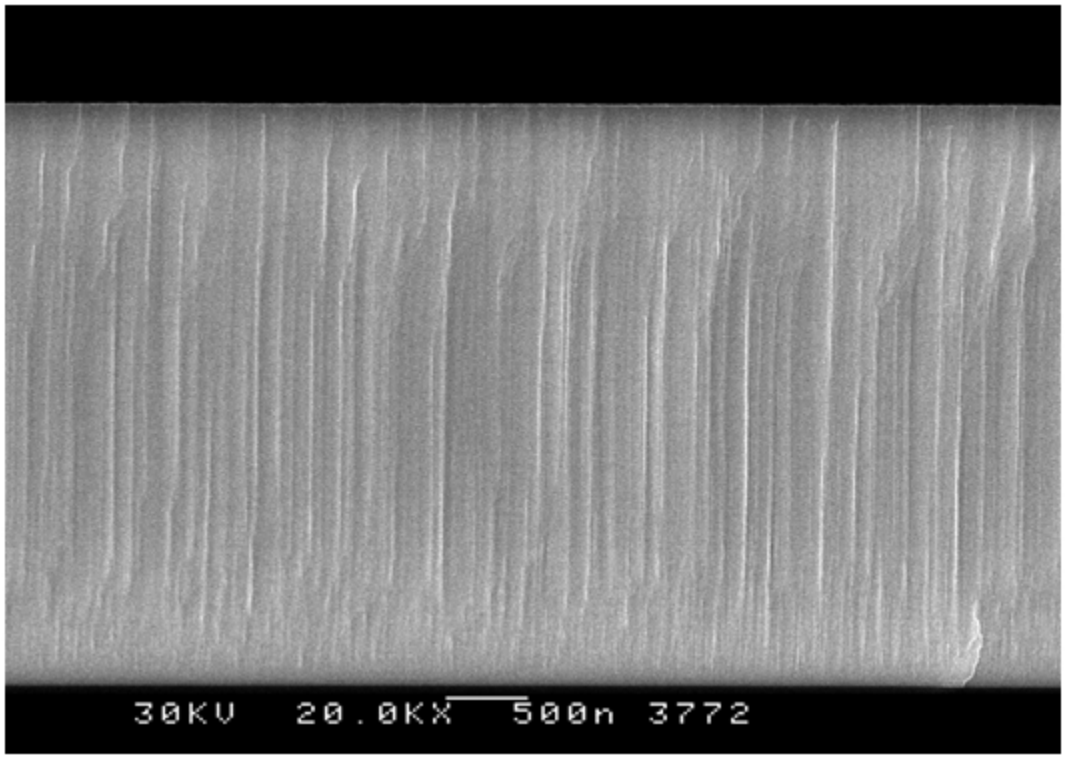


**Figure 6: SEM microstructure comparison of Ta depositions using the MPP process using Pulse 1 and conventional DC sputtering process at -30V substrate bias: DC magnetron deposited Ta film.**

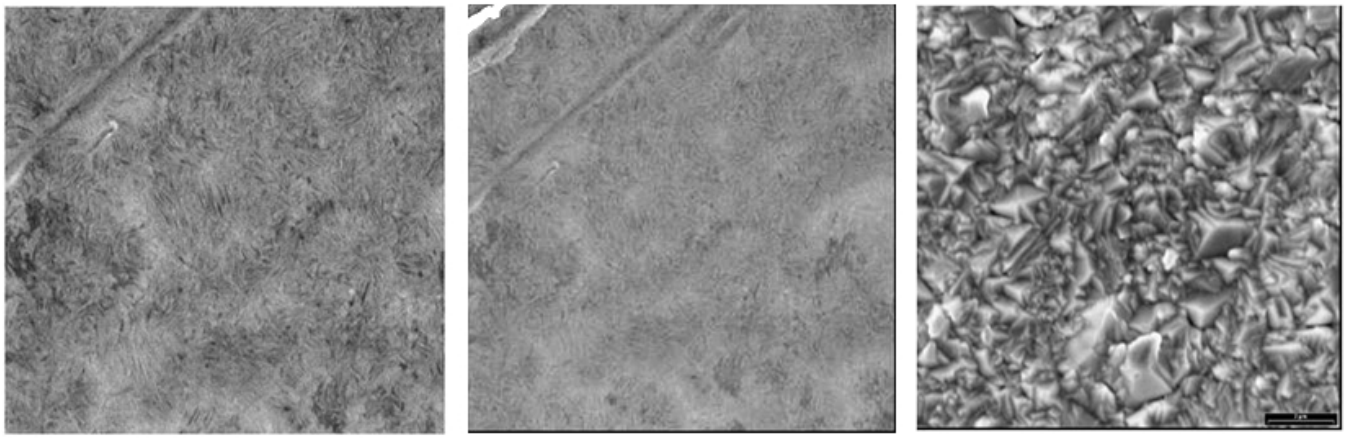

**Figure 7: SEM topography of MPP Ta deposition compared to DC magnetron deposition: S4 at 15,000X (left); S4 at 8,000X (middle); DC magnetron sputtered Ta on A723 steel with no bias at 8,000X (right).**

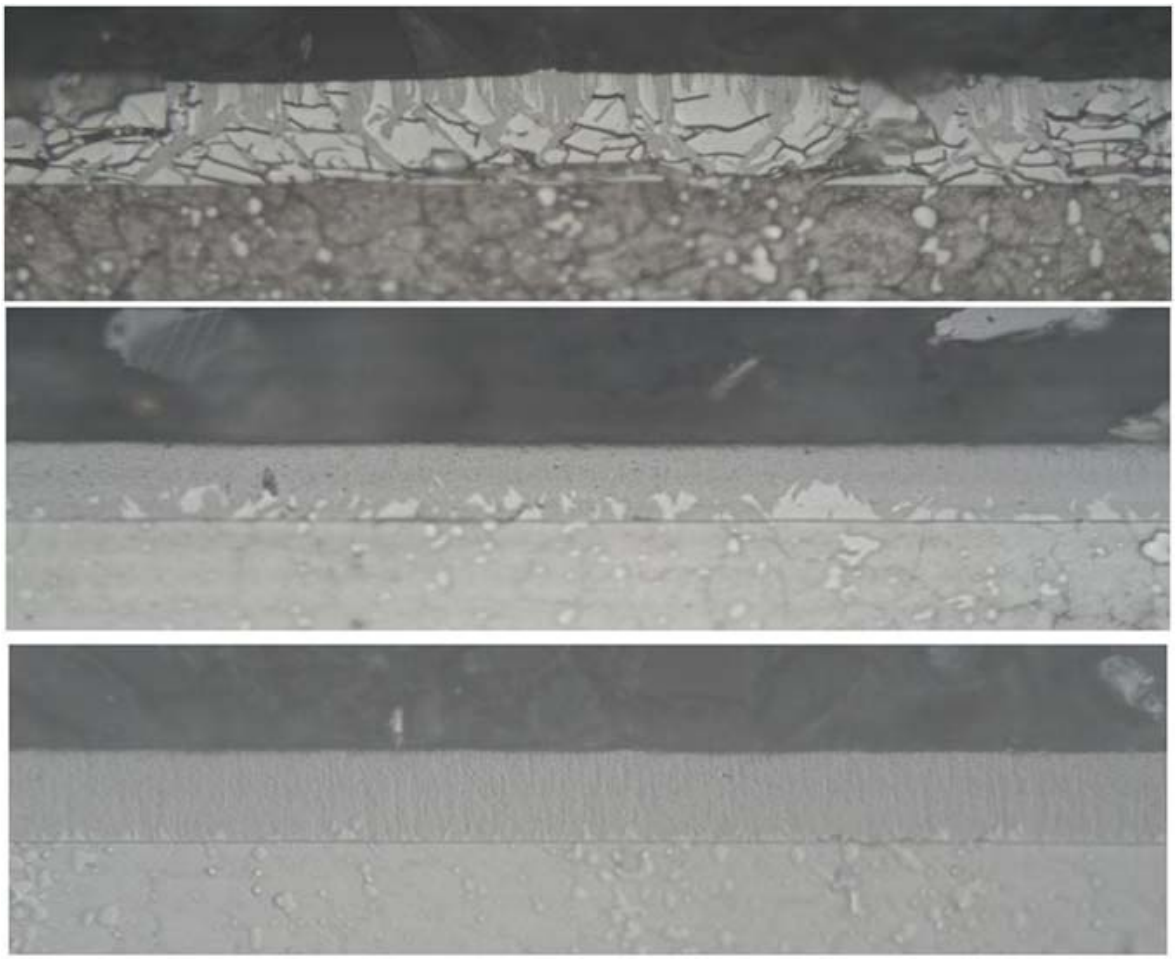

**Figure 8: SEM microstructure of MPP Ta depositions showed effect of substrate bias voltage on taltalum phase formation using Pulse 1: 1) Sample S1 deposited at -30V; 2) Sample S2 deposited at -40V; 3) Sample S4 deposited at -50V showing two coating areas**

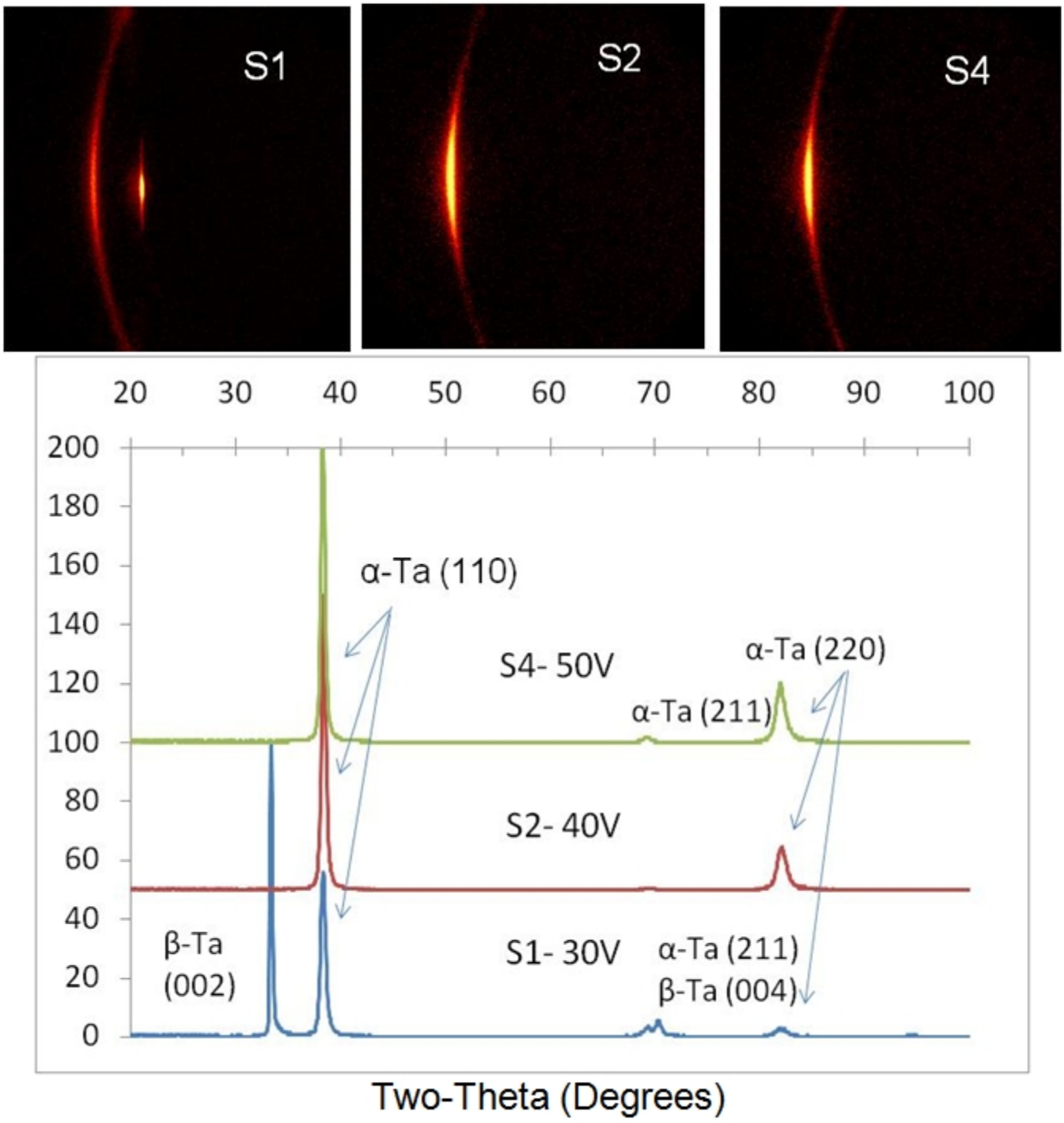


**Figure 9: XRD showing Debye rings for samples S1, S2, S4. S1 is a mixed phase coating: the left ring is α-Ta (110); the right ring section is highly textured β-Ta (002) reflection. S2 and S3 have predominately α-Ta, showing the Ta (110) ring.**